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No. VIII.

An Account of some Experiments made on Crude Platinum, and a New Process for separating Palladium and Rhodium from that Metal. By Joseph Cloud.—Read November 3d, 1809.

NATIVE Platinum, as we receive it from South America, is a heterogeneous compound, generally mixed with a considerable quantity of ferruginous sand, very sensibly attracted by the magnet; such, at least, was the specimen,—the subject of my experiments. In order, therefore, to free it as much as possible from the ferruginous mixture, I used the magnet as long as any thing could be separated by that means. Having thus far freed it from extraneous matter, it was submitted to the following treatment.

Process 1st. The crude Platinum was subjected to the action of boiling in nitro-muriatic acid (composed of an equal quantity, by measure, of the nitric and muriatic acids) until no further action took place. The acid, now holding Platinum, Palladium, Rhodium, Iron, and perhaps some other metals in solution, was decanted from the undissolved residue; which, according to Mr. Tenant, contains iridium and osmium.

Process 2d. To the solution from process 1st, I added a saturated solution of muriate of ammonia in boiling water, until no further precipitation of platinum took place; taking

care to separate the fluid from the precipitate as soon as possible, to prevent the precipitates of palladium and rhodium from mixing with the platinum; these metals being also precipitated by muriate of ammonia, although not with so much facility as the platinum. The precipitate was well washed with pure water, and the washings added to the decanted fluid.

Process 3d. The last precipitate, being an ammoniacomuriate of platinum, was heated to ignition, for the purpose of separating the muriate of ammonia, and was again dissolved in the nitro-muriatic acid, and precipitated in the same way, and with the same precaution observed in the last process. I now had a beautiful orange-coloured precipitate; which, on being heated to a white heat in a crucible, adhered together, was perfectly metallic, and very brilliant; and when fused by united streams of oxygen and hydrogen gas, it was very malleable and ductile; so that by means of rollers it was reduced into extremely thin plates: its specific gravity, in distilled water at 62° Fahrenheit, by a balance sensible to $\frac{1}{1000}$ part of a grain, was 23.543.

Process 4th. The acids and washings from process 2d and 3d, still holding a portion of platinum, and all the metals that were combined with it (except the osmium and iridium) in solution, were mixed together; and the platinum, palladium, rhodium, and perhaps small portions of other metals, were precipitated in a metallic form, by plates of zinc.—The precipitate was washed and dried.

Process 5th. The precipitate from the last process was combined with four times its weight of fine silver, and couppelled with a sufficient quantity of lead, for the purpose of destroying any of the base metals that were thrown down by the zinc. I had now a compound of silver, platinum, palladium, rhodium, and perhaps a small portion of gold.

Process 6th. The metals from process 5th, were reduced to thin plates, and submitted to the action of boiling nitric acid, until the silver and palladium were dissolved, and the acid ceased to operate: the solution was decanted, and the remaining metals were well washed, to free them from the

solution of silver.—This is a necessary precaution, for if any of it were suffered to remain, it would form a muriate of silver in the subsequent process, and impede its operations.

Process 7th. To the solutions and washings from the last process, I added pure muriatic acid to excess, and the silver was thrown down in form of muriate of silver. The acid, holding now nothing but palladium in solution, was decanted; the precipitate washed, and the washings added to the decanted fluid. From this the palladium may be precipitated, either by pure pot-ash, or prussiate of mercury, and the precipitate fused with borax. By the above processes, pure ductile palladium was obtained; its specific gravity in river water at 64° Fahrenheit, was $11.\frac{4}{5}$.

Process 8th. The undissolved metals from process 6th, being platinum, rhodium, and perhaps gold, were subjected to the action of nitro-muriatic acid, assisted by heat, until no further solution could be obtained. The platinum, and gold if any was present, were dissolved; and the rhodium remained in the form of a black powder. The solution was decanted, and the powder washed; which, on being heated to a white heat, assumed a metallic brilliancy, and was completely fused by the hydro-pneumatic blow pipe, at about 160° of Wedgewood. Its specific gravity 11.2 .

The rhodium thus obtained, very much resembles cast iron in colour; and, like it, is rigid and friable under the hammer. It is not acted on, either by the nitric or nitro-muriatic acids. As the principal object of this memoir is to communicate a new method of obtaining rhodium from its native combination, for a fuller account of the characters and properties of this metal, the reader is referred to the Transactions of the Royal Philosophical Society of London for 1804, page 428.

Process 9th. The platinum and gold may be obtained from the last solution, through the agency of muriate of ammonia, and sulphate of iron.

It is an extraordinary fact, first discovered by Dr. Wollaston, and fully confirmed by my experiments, that rhodium in an uncombined state, and in some of its combinations with

other metals, is insoluble in the nitric and nitro-muriatic acids. It is particularly remarkable, that it should be soluble in its native combination with crude platinum, and become insoluble in the artificial compound produced by process 5th. These phenomena may probably be accounted for by supposing that the platinum, palladium and rhodium, in a state of nature, were in *perfect* chemical combination ; the effect of reciprocal attraction. That is, the different metals were united together so intimately by chemical affinity, that each integral particle consisted of the same principles, combined in the same relative proportions, as in the general mass, united by the force of aggregation : the platinum and palladium being dissolved by the nitro-muriatic acid in process 1st, the force of aggregation, and the chemical attraction of the integrals are both destroyed ; and the rhodium, which perhaps did not form more than $\frac{1}{70}$ part of each integral ; becomes so extremely divided, that it is rendered susceptible of being oxidated, and dissolved by that agent.

There are numerous examples in chemistry, in which aggregation in bodies is so powerful that they are not sensibly acted on by others, even in the fluid state ; though the combinations of them are affected when the aggregation of the solid is destroyed : the native oxide of tin resists the action of any acid. This apparent insolubility is owing to its strong aggregation ; when this is overcome by mechanical operations, it becomes soluble. The ruby, the sapphire, and the adamantine spar, from the strength of aggregation, are scarcely affected by any chemical agent ; but if their cohesion be destroyed, they are then acted on. Hence the mechanical operations of trituration, levigation, and granulation, are of importance in facilitating chemical action ; partly by diminishing aggregation, and partly by increasing the surface on which action is exerted.

In the artificial compound of process 5th, the metals were in the state of *imperfect* chemical combination ; the integrant and constituent particles of the compound were substances differing in their nature from each other, and from the general

mass; which was composed by their being united by the force of aggregation, and presenting distinct surfaces to the action of their respective solvents. This appears evidently to be the case in a combination of gold and silver, and platinum and silver; for all compounds of these metals are soluble by alternate treatment with the nitric and nitro-muriatic acids.— If two parts of silver, intimately mixed with one part of gold, and reduced to a thin plate, be subjected to the action of dilute nitric acid, the silver will be dissolved without altering the form of the plate, other than rendering it extremely porous; cavities having been formed in the plate corresponding to each integral of the silver that was in the compound: Consequently, the silver and palladium would be taken up by the nitric acid in process 6th, and the platinum and gold by the nitro-muriatic in process 8th, without a solution of the rhodium taking place; its integral aggregation being superior to the chemical action of the acids.

How nature forms the immense variety of compounds which we are unable to imitate by art, and how far I have succeeded in illustrating these phenomena, I must leave for others to decide: as a humble labourer in the science of Analytical Chemistry, I have with much diffidence submitted these theories to the public eye, from a hope that they will draw forth a better explanation from some abler hand.